

Characterization and quantification of biochar alkalinity

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ABSTRACT

Lack of knowledge regarding the nature of biochar alkalis has hindered understanding of pH-sensitive biochar-soil interactions. Here we investigate the nature of biochar alkalinity and present a cohesive suite of methods for its quantification. Biochars produced from cellulose, corn stover and wood feedstocks had significant low- pK_a organic structural (0.03 to 0.34 meq g^{-1}), other organic (0 - 0.92 meq g^{-1}), carbonate (0.02 - 1.5 meq g^{-1}), and other inorganic (0 - 0.26 meq g^{-1}) alkalinities. All four categories of biochar alkalinity contributed to total biochar alkalinity and are therefore relevant to pH-sensitive soil processes. Total biochar alkalinity was strongly correlated with base cation concentration, but biochar alkalinity was not a simple function of elemental composition, soluble ash, fixed carbon, or volatile matter content. More research is needed to characterize soluble biochar alkalis other than carbonates and to establish predictive relationships among biochar production parameters and the composition of biochar alkalis.

KEYWORDS

Biochar; alkalinity; pH; functional groups; carbonate; organic

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Abbreviations FC = fixed carbon; VM = volatile matter; CEC = cation exchange capacity; XRF = x-ray fluorescence; XRD = x-ray diffraction

1. Introduction

Biochars, the solid co-products of the pyrolysis biomass-to-bioenergy pathway suitable for use as a soil amendment (Lehmann et al., 2006; Schimmelpfennig and Glaser, 2012), are diverse materials with a wide range of chemical and physical properties (Brewer et al., 2011; Kloss et al., 2012; Singh et al., 2010; Wang et al., 2014). Application of biochar to soil can sequester carbon (C) by both increasing soil carbon directly and by increasing yields of biomass C, but such benefits are dependent on properties of both the soil and the biochar. Biochar application has been shown to increase soil cation exchange capacity (CEC), water-holding capacity, nutrient retention, and pH, and also to decrease soil bulk density and net greenhouse gas emissions from soil agroecosystems (Fidel, 2015; Joseph et al., 2010; Laird et al., 2010). However, the effects of biochar amendments on soils arise from many complex-interactive processes, often resulting in strongly context-specific and method-dependent results (Joseph et al., 2010; Simek and Cooper, 2002). Alkalinity is one of the most influential biochar properties, because changes in pH have cascading impacts on many soil processes, including nitrogen mineralization, mineral precipitation, ion exchange, and greenhouse gas emissions (Joseph et al., 2010; McCormack et al., 2013). Many studies have shown that biochar amendments increase and buffer soil pH, but the nature of biochar alkalis, the influence of feedstock and biochar production conditions on biochar alkalinity, and the variability of alkali properties among biochars remain poorly understood (Xu et al., 2012; Yuan et al., 2011a, 2011b). A mechanistic understanding of how

specific biochar alkalis interact with soil is therefore imperative to further pH-related biochar research.

Four broad categories of biochar alkalinity have been identified in the literature: surface organic functional groups (as conjugate bases), soluble organic compounds (also conjugate bases of weak acids), carbonates (salts of bicarbonate and carbonate), and other inorganic alkalis, which may include oxides, hydroxides, sulfates, sulfides, and orthophosphates (Cheah et al., 2014; Singh et al., 2010; Yuan et al., 2011a). Distinguishing between these categories is essential to understanding the short- and long-term impacts of biochar on soil pH, because soluble organic and inorganic alkalis contribute to short-term acid amelioration (Silber et al., 2010; Yuan et al., 2011b); while surface organic functional groups contribute to long-term soil CEC and pH buffering capacity (Mao et al., 2012). Furthermore, biochar surface functional groups with pK_{as} close to that of typical soil pHs (5 to 7) will be the most active ion donators and acceptors in soil.

Widely differing methods for defining and quantifying biochar alkalinity categories have been employed in previous experiments, thereby confounding comparisons among studies (Dai et al., 2014; Singh et al., 2010; Wan et al., 2014; Yuan et al., 2011b; Yuan and Xu, 2011). Existing methods for determining total alkalinity include: (1) directly titrating a biochar-water slurry with 0.1 M HCl (Wan et al., 2014), (2) equilibrating biochar with 0.03 M HCl and titrating the extracts with NaOH (Yuan and Xu, 2011), and (3) shaking biochar with 1 M HCl for 2 h, followed by titration of extracts with NaOH (Singh et al., 2010). Determining carbonate alkalinity in biochars typically requires quantification of CO_2 liberated during equilibration with HCl by using a manometer or NaOH trap. However, recommended HCl concentrations have varied from 1 to 4 M and equilibration times have ranged from 1 to 5 days (Wan et al., 2014; Wang et al., 2014). The NaOH trap method was determined to be the most accurate for

quantification of carbonates, but the effects of HCl concentration and equilibration time on carbonate and total alkalinity determination have not been examined (Wang et al., 2014). Silber et al. (2010) showed that the release of ions and neutralization of H^+ by biochar is both pH- and time-dependent, signifying total alkalinity and carbonate alkalinity should be measured under the same conditions to facilitate quantitative comparisons; however, no single study has done so. Lastly, most studies use Boehm titrations to quantify weak organic acid functional groups that are directly bonded to biochar surfaces. These functional groups can contribute to alkalinity when present as deprotonated conjugate bases. On the other hand, recent reports indicate that soluble alkalis can confound Boehm titration results (Fidel et al., 2013; Tsechansky and Graber, 2014). Although several studies have quantified one – and in some cases two – categories of biochar alkalinity (Chen et al., 2015; Chun et al., 2004; Dai et al., 2014; Tsechansky and Graber, 2014; Wan et al., 2014; Wang et al., 2014; Yuan et al., 2011b), no study has systematically investigated the relative abundance of all four categories of biochar alkalinity or considered method efficacy. Therefore, this study investigates the nature of biochar alkalis and presents a cohesive suite of methods for their quantification.

2. Materials and Methods

2.1. Biochar preparation

Given the diversity of biochars, a full analysis examining biochars produced from all possible combinations of feedstock and pyrolysis conditions is beyond the scope of this study. Hence, eight biochars produced at three temperatures (300, 500 and 600°C) and by three processes (slow pyrolysis, fast pyrolysis, and gasification) were chosen to encompass the anticipated range of total alkalinity and alkalinity distributions for cellulosic and lignocellulosic feedstocks (Table 1).

Slow pyrolysis biochars made from cellulose (Sigma Aldrich) and corn stover (*Zea mays*; harvested in Boone, IA) were pyrolyzed in a N₂-purged muffle furnace. The muffle furnace temperature was first held at 105°C for 1 hour to remove any water present in the feedstock, then the furnace was heated to 100°C below the highest treatment temperature (200°C, 400°C or 500°C) at 10°C per minute, and held at that temperature for 2 hours before increasing to the highest treatment temperature at 0.5°C per minute. The highest treatment temperature (300°C, 500°C, or 600°C, see Table 1) was then maintained for 2 hours before the furnace was allowed to cool overnight under N₂-purge. A hardwood slow pyrolysis biochar (HW5s), obtained from Royal Oak Enterprises, LLC (size #10 charcoal, 0.5-2mm, <http://royal-oak.com/>), was produced using a traditional kiln. A mixed wood gasification biochar (MW6g), obtained from ICM, Inc. (<http://www.icminc.com/>), was produced using an auger bed gasifier at 550-650°C from a blend of primarily oak (*Quercus* spp.), elm (*Ulmus* spp.) and hickory (*Carya* spp.) woodchips with particle sizes 0.1 – 2000 mm. Two fast pyrolysis biochars, RO5f and CS5f – produced from red oak wood (*Quercus rubra*) and corn stover (*Zea mays*) respectively at 500°C – were obtained from the Center for Sustainable Energy Technologies at Iowa State University. Both of the fast pyrolysis biochars were produced in a fluidized bed reactor that used N₂ as a carrier gas and sand particles (0.5 mm average particle diameter) as fluidization media (Pollard, 2009; Pollard et al., 2012). These fast pyrolysis biochars were sieved to <0.50 mm to minimize the influence of sand particles. All slow pyrolysis and gasification biochars were ground to <0.50 mm to minimize the influence of particle size on chemical analyses.

2.2. Biochar pH

Biochar pHs were measured in duplicate by mixing biochar and deionized water in a 10:1 water:biochar (mL:g) ratio; the resultant slurries were equilibrated for 1 hr, and then the pHs

were measured by placing a glass H⁺ electrode in the solution just above the settled biochar. Biochar pH in NaCl was measured by equilibrating 0.3 g of each biochar with 15 mL of 1 M NaCl for 24 h on a shaker table. The samples were then filtered to <0.45 µm, and the pH of each NaCl extract was analyzed (Table 1).

2.3. Proximate analysis

Ash, fixed carbon (FC), and volatile matter (VM) of untreated and acid-washed biochars were quantified in triplicate by thermogravimetric analysis using a Mettler TGA/DSC 1 (approach adapted from the standard ASTM method) (Choi et al., 2014). Biochar samples weighing 10-20 mg were heated to 105°C and held at that temperature for 40 min to remove water. Then samples were heated to 900°C in an N₂ atmosphere at a rate of 10°C min⁻¹; next the temperature was held at 900°C for 20 min; and lastly the samples were exposed to air at 900°C for 30 min. VM and FC were determined as the percentage of mass lost under N₂ purge and after exposure to air for 30 min at 900°C, respectively. Ash content was determined as the percentage of the initial mass remaining after the sample had been exposed to air at 900°C. To compare the amounts of ash and VM removed during acid washing, the ash and VM contents were normalized to the FC content. The acid-soluble ash was calculated as the difference between FC-normalized ash value of the untreated and acid-washed biochars. Acid-soluble VM was determined similarly. This calculation was based on the assumption that FC is not acid-soluble.

2.4. Total elemental analysis

C, H, and N of the biochars were determined in triplicate using a Vario Microcube (Elementar) combustion analyzer (Table S1). Additional elements of interest were determined by x-ray fluorescence (XRF) spectroscopy using a Philips PW 2404 X-ray spectrometer (XRF) equipped

with a rhodium X-ray tube operated at 3600 watts (Lawrinenko et al., 2016). The spectrometer was flushed with helium during all measurements. All measurements were corrected for tube drift by monitoring samples (AUSMON-silicate minerals reference monitor and CA69, a carbonate rock reference monitor). Specimens were presented to the spectrometer as 2 g of loose powders in disposable sample cups sealed with polypropylene film (6- μ m thick). Calibration standards were prepared by spiking a low-ash biochar derived from cellulose slow-pyrolyzed at 700 °C (prepared in the same manner as slow pyrolysis corn stover biochars) with different percentages of reagent grade potassium chloride and standard reference materials derived from coal ash, minerals and wood (NIST 1633a, NIST 2691, USGS Nod-A-1, NIST 2910, and AWP Std I; see Table S2). These mixtures were combined and co-ground in a SPEX Shatterbox puck mill for two minutes. Due to the similarity between the CE5s and the cellulose biochar used to make the calibration standards, CE5s was excluded from XRF analysis.

2.5. X-ray diffraction

X-ray diffraction patterns of four untreated and acid-washed biochars (CS5f, CS3s, CS6s and MW6g) were obtained with an x-ray diffractometer equipped with a graphite monochromator using Cu K α radiation generated at 40 KV and 30 mA. Diffracted photons were detected by a scintillation counter in step-scan mode with a step size of 0.05° 2 θ and a dwell time of 7 seconds per step. The divergence slit was fixed at 0.5° and the anti-scatter slit was fixed at 1.5°. Random powder mounts of biochars were analyzed at ambient temperature and humidity. Peaks and corresponding minerals were identified using JADE™ 9.0 software.

2.6. Total alkalinity and ion release

Total alkalinity was quantified by reaction with HCl and subsequent back titration (Fidel, 2012). This method was previously shown to be effective for use with lignocellulosic biochars, but may need adjustment for use with biochars derived from other feedstocks such as manure. Briefly, the optimal reaction time and pH were assessed by comparing the amounts of protons accepted and ions solubilized after shaking with HCl solutions for 2, 4, 8, 16, 24, 48 and 72 hours at pH of about 1, 2 or 3 from three of the biochars (CE5s, RO5f and CS5f). Biochar was first shaken rapidly on an automatic shaker table with the appropriate HCl solution at a 50:1 solution:biochar (v:w) ratio. Biochar-solution slurries were then filtered to $<0.45\ \mu\text{m}$, and the extracts were titrated to pH 8.2 (phenolphthalein indicator) with standardized 0.05 M NaOH. The 0.05 M HCl solution was also titrated as a blank. Total alkalinity, expressed as mmol of H^+ reacted per gram of air-dry biochar, was calculated from the difference between the amount of acid titrated in the sample and the blank. To quantify elements released during reaction with HCl, triplicate acidic extracts for each biochar were analyzed for Na, K, Ca, Mg, Si, S, P, Fe, Al, and Mn using a Thermo Scientific™ iCAP™ 7400 ICP-OES Analyzer. The optimal reaction conditions were determined to be 72 hours at pH ~ 1.3 to 2, and therefore the remaining biochars were equilibrated with 0.05 M HCl for 72 h ($1.3 \leq \text{pH} \leq 2$). Two biochars, HW5s and MW6g, increased the final solution pH to >2 , and so these biochars were equilibrated at a 100:1 solution:biochar ratio.

2.7. Structural and other organic alkalinity

We define “organic alkalinity” as the equivalents of organic functional groups in biochar that are capable of accepting protons, including both functional groups directly bonded to biochar’s condensed aromatic matrix and functional groups in acid-soluble organic compounds. We define “structural alkalinity” as the concentration of such organic functional groups that are directly

bonded to a biochar's aromatic carbon framework and that are protonated after equilibration with 0.05 M HCl. In principle, the 0.05 M HCl solution used to quantify total alkalinity should react with all functional groups with pK_a s between the pH of the biochar-equilibrated HCl (1.3-2.0) and the initial biochar pH prior to the addition of HCl (Table 1). The Boehm titration, in which surface functional groups are quantified by equilibration with NaHCO_3 , Na_2CO_3 and NaOH , is capable of quantifying conjugate acids within discrete pH ranges defined by the pK_a s of the reactants (5-6.4, 6.4-10.3 and 10.3-13, respectively) (Boehm, 1994; Goertzen et al., 2010). Only functional groups with conjugate acid pK_a s less than that of the initial biochar pH are expected to accept protons upon addition of acid to biochar; we therefore refer to conjugate bases of acidic functional groups with $pK_a < \text{biochar pH}$ as “organic alkalis.” However, the lignocellulosic biochars in this study support aqueous-phase pHs ranging from 7.1-10.3, and hence the functional group concentration within the 6.4-to-biochar pH range cannot be quantified using the Boehm titration. Therefore, we have subdivided “organic alkalis” into the following categories: (1) *structural alkalis* directly bound to condensed aromatic C with conjugate acids having pK_a s ranging from 5.0 to 6.4, and (2) *other organic alkalis*, whose conjugate acids include both functional groups with pK_a s between 6.4 and the biochar pH, and soluble organic acids such as acetic or formic acids (Lin et al., 2012; Liu et al., 2015). The *other organic alkalis* category may also include conjugate bases of weak acids with $pK_a < 5$, and/or condensed aromatic C itself which may directly adsorb H^+ , the latter of which – based on studies of H^+ sorption by graphite – should be negligible (Boehm, 1994).

Biochar surface functional groups were quantified in triplicate using the integrated “sparge-barium-barium” Boehm titration method developed specifically for biochars by Fidel et al (2013). This method was chosen because it accounts for functional groups with $pK_a > 6.4$ found

on organic compounds that are soluble in Na_2CO_3 and NaOH (Graber et al., 2016). Briefly, biochars were pre-treated to remove acid-soluble alkalis by washing with 0.05 M HCl , followed by CaCl_2 and water. Then the standardized Boehm titration procedure developed by Goertzen et al (2010) was used to quantify functional groups with pK_a values between 5.0 and 6.4, or “*low- pK_a structural alkalis*.” To quantify functional groups with pK_a s >6.4 and >10.3 , 0.05 M Na_2CO_3 and NaOH extracts (respectively) were centrifuged with BaCl_2 to remove dissolved organic compounds and carbonates prior to acidification and titration with NaOH (Fidel et al., 2013). Although functional groups in the higher pK_a ranges (6.4-10.3 and 10.3-13) were not used to directly quantify other organic alkalis, we quantify them here to give perspective to the determination of other organic alkalis. Other organic alkalis were quantified as the total alkalinity minus the sum of structural alkalis, carbonates ($\text{CO}_3^{2-} + \text{HCO}_3^-$), and other inorganic alkalis.

2.8. Carbonate alkalinity

Total biochar carbonates ($\text{CO}_3^{2-} + \text{HCO}_3^-$) were quantified in triplicate using a modified NaOH trap method (Fidel, 2012). Briefly, 2 g of each biochar (or 1 g of HW5s and MW6g, see section 2.6) were stirred with 100 mL of 0.05 M HCl in a container placed inside a sealed Mason jar; a separate container inside of the Mason jar held 15 mL of 1 M NaOH . The HCl was added using a syringe through a grey butyl septa to ensure no CO_2 escaped from the biochar prior to closing the Mason jar. After 72 h, the NaOH trap was removed, 15 mL of 1 M BaCl_2 were added to the NaOH , and the solution was titrated with 1 M HCl to pH 8.2 (phenolphthalein indicator) to quantify the amount of CO_2 evolved from the biochar.

The quantities of CO_3^{2-} and HCO_3^- in the total biochar carbonates (determined above) were determined based on the pH and total carbonate content of NaCl extracts (see section 2.2). A small aliquot (0.1 or 0.2 mL) of each NaCl biochar extract was pipetted into a 6 mL Exetainer vial, the headspace was flushed with He gas, and then 0.1 mL of 3 M H_3PO_4 was added to convert carbonates to CO_2 . A gas sample from the vial headspace was then analyzed for CO_2 using a gas chromatograph. The $\text{CO}_3^{2-}:\text{HCO}_3^-$ ratio of the NaCl-soluble carbonates was estimated from the NaCl extract pH and the pK_a of bicarbonate (10.3) using the Henderson-Hasselbach equation. This approach assumes that all HCO_3^- was soluble in NaCl, and all NaCl-insoluble carbonates were present as CO_3^{2-} ; thus the CO_3^{2-} content of the biochars was calculated as the difference between total CO_2 measured using the NaOH trap technique and the bicarbonate concentration.

2.9. Other inorganic alkalinity

“Other inorganic alkalinity” is here defined as the quantity of protons consumed by acid-soluble inorganic compounds in biochar such as phosphate, sulfate, silicate, iron hydroxides, and aluminum hydroxides. Other inorganic alkalinity was estimated as the sum of P, S, Si, Fe and Al species solubilized during reaction with 0.05 M HCl, in meq g^{-1} . The concentration of each element was converted to mmol g^{-1} of the expected alkali specie (PO_4^{3-} , SO_4^{2-} , SiO_2 , FeOOH , $\text{Al}(\text{OH})_3$, etc) (Lindsay, 1979), then converted to meq g^{-1} based on the pH of the biochar relative to the pK_a s of the alkalis’ conjugate acids (Table S3). Our definition of other inorganic alkalinity excludes any inorganic surface functional groups that accepted protons were not solubilized during the reaction with acid; if present in significant quantities, such groups would be included by difference in the “other organic alkalinity” category.

For biochars with a pHs between 7.1 and 7.3 (RO5f and CS3s), other inorganic alkalinity (in meq g⁻¹ of biochar) was calculated from element concentrations (in brackets) using the equation:

$$\text{Other inorganic alkalinity} = 1.5[\text{P}] + 0.5[\text{S}] + 2[\text{Fe}] + 3[\text{Al}] \quad (1)$$

And for biochars with pHs between 7.5 and 9.5 (CS5f, HW5s, and MW6g):

$$\text{Other inorganic alkalinity} = 2[\text{P}] + 0.5[\text{S}] + 3[\text{Fe}] + 3[\text{Al}] \quad (2)$$

Lastly, for biochars with pHs between 10.0 and 10.5 (CS5s and CS6s):

$$\text{Other inorganic alkalinity} = 2[\text{P}] + 0.5[\text{S}] + [\text{Si}] + 3[\text{Fe}] + 3[\text{Al}] \quad (3)$$

This estimation of other inorganic alkalinity assumes that oxides and hydroxides of base cations – such as CaO, KOH or Mg(OH)₂ – do not contribute significantly to biochar inorganic alkalinity. Although oxides and hydroxides of base cations have been posited as a hypothetical source of biochar alkalinity, they are not expected to form in appreciable quantities at temperatures lower than 700°C (Ar and Doğu, 2001; Galan et al., 2012), and their presence in biochars has not been verified (Keiluweit et al., 2010; Kloss et al., 2012; Lawrinenko and Laird, 2015; Silber et al., 2010; Yuan et al., 2011b). Thus, we consider it unlikely that the biochars analyzed in this study contain significant quantities of oxides or hydroxides of base cations, and we have not included them in our analysis of inorganic alkalis.

3. Results and Discussion

3.1. Evaluation of acid washing and total alkalinity quantification methods

Kinetics of H⁺ reaction and nutrient release from biochars at varying pHs was examined to determine the optimal HCl concentration and reaction time for determination of total alkalinity

(Figure S1). Equilibration of 0.05 M HCl with biochar by shaking for 24 to 72 h (50 mL acid:1 g biochar) consistently yielded the highest total alkalinity upon titration of the resultant extract relative to other HCl concentrations and equilibration times tested. No significant difference in HCl consumed was observed between 24 and 72 h equilibration times. Use of HCl concentrations less than 0.05 M resulted in lower estimations of total alkalinity due to incomplete reaction of HCl with biochar alkalis at $\text{pH} > 2$. Using higher concentrations of HCl, such as 0.1 M or 1 M, also resulted in lower estimates of biochar alkalinity, likely due to the dissolution of acid-soluble alkalis at $\text{pH} \leq 1$ and subsequent interference with the titration of the extracts. Furthermore, we observed that quantities of CO_2 evolved were sensitive to HCl concentration, and therefore recommend using the same concentration of HCl for total alkalinity and carbonate alkalinity to ensure the measurements are comparable (Figure S2). Therefore, *total alkalinity* is here defined as the capacity of untreated biochar to accept protons from a 0.05 M HCl solution ($1.3 \leq \text{pH} \leq 2$) during a 72 h equilibration, and *carbonate alkalinity* is defined as the amount of CO_2 evolved during this reaction; both are reported as meq g^{-1} .

To confirm that shaking biochars with 0.05 M HCl was sufficient to remove crystalline alkali species, select untreated and acid washed biochars (CS5f, CS3s, CS6s, and MW6g) were analyzed using XRD (Figure S3). Following acid washing, XRD peaks attributed to sylvite, calcite, natrite, dolomite, and/or butschliite were either no longer observable or greatly diminished in intensity. The absence of these peaks suggests that the acid washing procedure removed the majority of soluble, mineral-phase alkalis. Comparison of acid-extractable and total element concentrations revealed that a significant proportion of metals and metalloids are acid-insoluble, likely due to occlusion within insoluble moieties such as quartz, and are therefore unlikely to contribute to total alkalinity. Overall, mineral phases observed in the biochars were

consistent with literature reports (Kloss et al., 2012; Yuan et al., 2011b). Therefore, we conclude that washing with HCl ($1.3 \leq \text{pH} \leq 2$) followed by two CaCl_2 washes and four H_2O washes (50 mL:1 g biochar:solution ratio) is sufficient to remove soluble crystalline alkalis.

3.2. Total alkalinity

Total alkalinities varied widely among biochars ($0.23\text{--}2.70 \text{ meq g}^{-1}$), with MW6g and CE5s having the highest and lowest total alkalinities, respectively (Figure 1). Slow pyrolysis corn stover biochars exhibited increasing total alkalinity with increasing pyrolysis temperature. Total alkalinity was not significantly correlated with total element concentrations (C, H, N, S, P, Al, Fe, Mn, Na, K, Ca or Mg), any of the proximate analysis metrics (insoluble ash, soluble ash, insoluble VM, soluble VM, or FC), or ratios thereof (Figure S4, Tables S1, S4 and S5). However, total alkalinity was strongly correlated with total equivalents of acid-soluble base cations ($r^2 = 0.83$) (Figure 2). Furthermore, biochar pH measured in water increased with increasing total alkalinity and increasing proportions of acid-extractable K and Na relative to Ca and Mg (Tables 1-2 and Figure 1). For example, CS6s had the highest monovalent-to-divalent base cation equivalent ratio (2.5:1), the second highest total alkalinity, and the highest pH; MW6g on the other hand, had the highest total alkalinity but a lower monovalent-to-divalent cation ratio (0.1:1), and consequently its pH was lower than CS6s. Measuring pH in 1 M NaCl instead of water did not remove the effect of base cations (Table 1). Thus, among the lignocellulosic biochars examined here, biochar alkalis were predominantly associated with base cations, and higher proportions of acid-soluble monovalent cations among total base cations corresponded with higher biochar pHs. The observed relationship between pH and total alkalinity demonstrates that pH should not be used as a proxy for biochar alkalinity, due to the influence of base cations on alkali solubility.

3.3. Organic alkalinity

Boehm titrimetry estimates the concentrations of acidic surface functional groups, which contribute to total alkalinity when their deprotonated conjugate bases accept protons upon exposure of biochars to acid. However, comparison of Boehm titration results with total alkalinity can become problematic because Boehm titrations only quantify functional group concentrations within discrete pK_a ranges (defined by the conjugate acid pK_a s of the reactants $NaHCO_3$, Na_2CO_3 and $NaOH$), whereas total alkalinity includes all sources of alkalinity which are reactive up to the pH of biochar equilibrated in distilled water (biochar pH). Hence, to distinguish surface functional groups which contribute to total alkalinity (conjugate acid $pK_a < \text{biochar pH}$) from those that do not ($pK_a > \text{biochar pH}$), we divide structural alkalinity into two categories: (1) structural alkalinity comprised of surface functional groups having $5.0 \leq pK_a \leq 6.4$ (“*structural alkalis*” contributing to “*low- pK_a structural alkalinity*”), and (2) structural alkalinity comprised of organic functional groups with $6.4 \leq pK_a \leq \text{biochar pH}$. Because the structural functional groups with $6.4 \leq pK_a \leq \text{biochar pH}$ cannot be distinguished from soluble organic alkalis with conjugate acids having $pK_a \leq \text{biochar pH}$, these are together considered *other organic alkalis*.

The majority of biochars had higher *low- pK_a structural* alkalinities than *other organic* alkalinities. The corn stover biochars tended to have higher low- pK_a structural alkalinities compared with wood biochars produced under similar conditions. Slow pyrolysis corn stover biochar pyrolyzed at 300°C had a higher structural alkalinity than biochars pyrolyzed at 500-600°C, demonstrating a pyrolysis temperature effect. Compared with slow pyrolysis biochars, fast pyrolysis biochars had higher low- pK_a structural alkalinities, suggesting that heating rate - in addition to pyrolysis temperature - may affect the formation of low- pK_a surface functional

groups. Biochars subject to faster heating rates may have higher structural alkalinities due to a lower extent of feedstock pyrolysis (Brewer et al., 2012, 2009; Sun et al., 2012). Thus both feedstock and pyrolysis conditions affected biochar structural alkalinity, although the effect of temperature appeared non-linear. These low-pK_a structural functional groups are of unique importance in that they contribute to long-term soil pH buffering capacity and CEC in addition to total alkalinity. Indeed, both Amazonian Terra Preta soils and Midwestern Mollisols have been shown to contain high concentrations of carboxylic acids associated with biochar-like black carbon residues, which may be substantial contributors to the organic matter-associated CEC of these soils (Mao et al., 2012).

The biochars pyrolyzed at 600°C (CS6s and MW6g) had the largest quantity of other organic alkalis, followed by the corn stover biochars produced at 300 and 500°C, whereas RO5f, HW5s and CE5s had negligible (≤ 0.02 meq g⁻¹) quantities of other organic alkalis (Figure 1). All biochars with concentrations of functional groups in the 6.4-10.3 pK_a range > 0.1 meq g⁻¹ and pH > 7.5 also had organic alkalinities > 0.1 meq g⁻¹ (Figure S5), suggesting that these functional groups contributed to other organic alkalinity in sufficiently alkaline biochars. Indeed, biochars with pHs approaching the pK_a of the Na₂CO₃ Boehm reactant (10.3), had functional group concentrations in the 6.4-10.3 pK_a range (0.25-0.35 meq g⁻¹) approaching their concentrations of other organic alkalis (0.49-0.50 meq g⁻¹). Furthermore, the biochars with pHs close to the pK_a of NaHCO₃ (6.4) had the lowest quantities of other organic alkalis (< 0.05 meq g⁻¹). Other organic alkalinity not accounted for by high-pK_a structural functional groups can probably be attributed to soluble organic alkalis such as acetate and formate, which have been previously identified in aqueous biochar extracts (Lin et al., 2012; Liu et al., 2015).

3.4. Carbonates and other inorganic alkalinity

The quantities of carbonates ($\text{HCO}_3^- + \text{CO}_3^{2-}$) and other inorganic alkalis varied greatly among the eight biochars (Figure 2). Carbonate alkalinity increased with increasing pyrolysis temperature among the slow pyrolysis corn stover biochars ($\text{CS3s} < \text{CS5s} < \text{CS6s}$), and with increasing divalent cation concentrations among all biochars. The amount of HCO_3^- in the biochars ranged from 0.01 to 0.27 meq g^{-1} , accounting for 2 to 100% of carbonate alkalinity; thus CO_2 evolved upon acidifying biochar cannot be assumed to originate entirely from one carbonate specie or the other (Table S7).

Concentrations of other inorganic alkalis – here defined as non-carbonate soluble inorganic alkalis and estimated using soluble metal and metalloid concentrations – ranged from 0-0.60 meq g^{-1} . Total inorganic alkalinity (carbonate and other inorganic alkalinity) of the slow pyrolysis corn stover biochars increased consistently with increasing pyrolysis temperature ($\text{CS3s} < \text{CS5s} < \text{CS6s}$).

3.5. Contributions of the various alkalis to total alkalinity

The contributions of the various alkalis to total alkalinity varied widely with respect to feedstock, pyrolysis temperature and heating rate. The cellulose biochar (CE5s) contained negligible ash (Figure S1) and hence its alkalinity was dominated by structural alkalis (87%; conjugate acid pK_a 5-6.4). For the lignocellulosic biochars, however, structural alkalinity ranged from 3 to 49% of total alkalinity. Other organic and inorganic alkalis consistently contributed <33% and <38% of the total alkalinity, respectively. Wood biochars consistently had a higher proportion of carbonate alkalinity than corn stover biochars, whereas corn stover biochars consistently had a higher proportion of other (non-carbonate) inorganic alkalinity. When combined, all inorganic alkalis consistently constituted a majority (55-95%) of lignocellulosic biochars' total alkalinity. Therefore, we conclude that all four categories of biochar alkalinity contribute to biochars'

capacity to react with acid, and that inorganic alkalis tend to dominate among wood and corn stover biochars.

3.6. Implications

We have identified four forms of biochar alkalinity – low- pK_a structural, other organic, carbonate, and other inorganic alkalinity – and quantified them in eight biochars. These biochars, derived from four feedstocks (cellulose, red oak, mixed wood, and corn stover) and three temperatures (300, 500 and 600°C), demonstrated a wide range of total alkalinity and diversity of alkali distributions. This diversity allows for development of biochars tailored to specific agricultural and environmental applications, including the amelioration of soil acidity and buffering the pH of composts and soil-less potting media. Indeed, we anticipate that analysis of biochars not included here, such as those produced from manure or other non-lignocellulosic feedstocks and those produced at different temperatures (such as 350–450°C, or >650°C), would reveal an even wider diversity of total alkalinities and distributions. Feedstock, pyrolysis temperature, and other pyrolysis conditions all affected biochar alkalinity and relative proportions of biochar alkalis. Inorganic alkalis consistently constituted the majority of total lignocellulosic biochar alkalinity, emphasizing their importance in pH-sensitive biochar research. Corn stover biochars consistently had higher structural alkalinities than wood biochars, suggesting that corn stover biochars will buffer soil pH and contribute to CEC more than wood biochars in the long term. However, variability of the impact of pyrolysis conditions and feedstock on biochar alkalinity and alkali composition suggest that biochar alkalinity may arise from complex interactions during production that are difficult to predict solely from pyrolysis parameters. A lack of consistent correlations between VM, FC or ash content and total alkalinity or alkali composition suggests that proximate analysis may be of little use for assessing biochar

alkalinity. Acid-soluble base cation concentration was an accurate proxy for total alkalinity among the biochars studied here, but this approximating total alkalinity alone does not provide insight into alkali composition or the contribution of biochar to soil pH buffering capacity or CEC. Total alkalinity and alkali distributions should therefore be directly quantified until the relationship between biochar alkalinity and other biochar properties is better understood.

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ASSOCIATED CONTENT

A. Supplementary material. Supplemental Figures S1-S6, Tables S1-S7, in-depth discussion of XRD results, and comparison of proximate analysis with functional group concentrations can be found online on the Chemosphere website.

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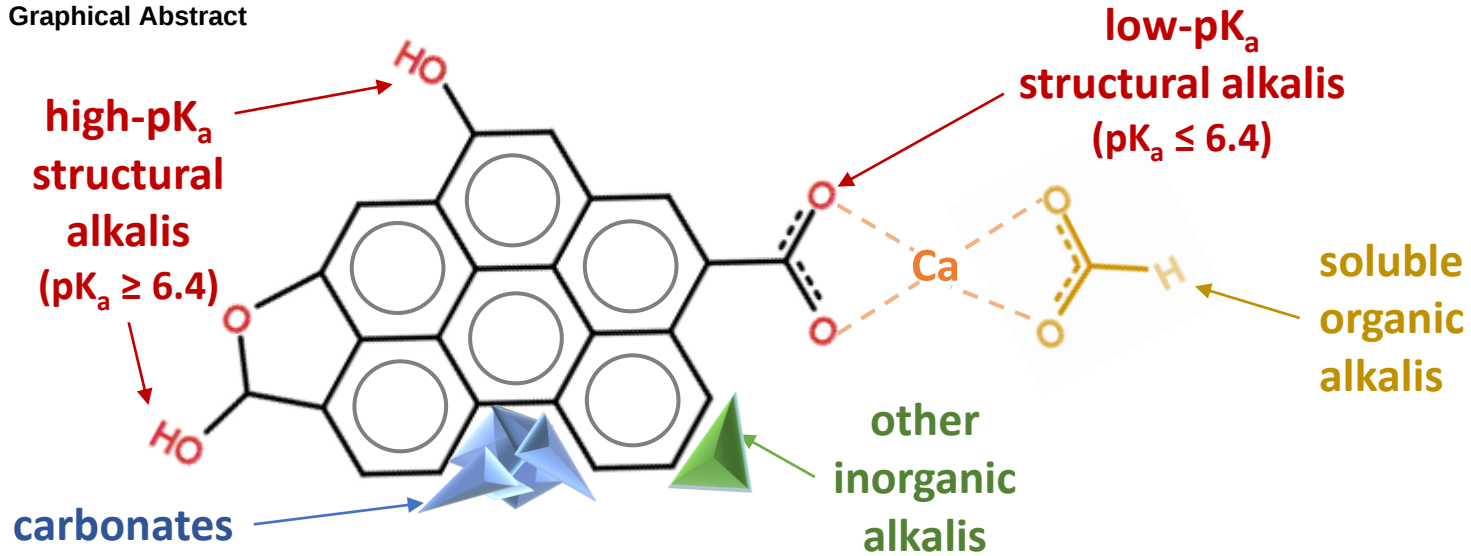
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Graphical Abstract



Characterization and quantification of biochar alkalinity: *Figures and Tables*

Table 1. Biochar abbreviation, feedstock, pyrolysis temperature, process type, and biochar pH (in H₂O and 1M NaCl) expressed as means of two replicates (± 0.1).

Biochar	Feedstock	T (°C)	Process	pH (H ₂ O)	pH (NaCl)
CE5s	Cellulose	500	Slow pyrolysis	6.4	6.4
RO5f	Red Oak	500	Fast pyrolysis	7.1	7.3
CS5f	Corn stover	500	Fast pyrolysis	8.4	7.6
CS3s	Corn stover	300	Slow pyrolysis	7.3	6.7
CS5s	Corn stover	500	Slow pyrolysis	10.1	9.2
CS6s	Corn stover	600	Slow pyrolysis	10.3	9.3
HW5s	Hardwood	~500	Slow pyrolysis	7.9	8.2
MW6g	Mixed wood	~600	Gasification	8.8	8.6

T = highest pyrolysis treatment temperature

Table 2. Concentrations of inorganic elements released from the untreated biochars after 72 hr reaction with 0.05 M HCl (n = 3).

Concentration (g kg ⁻¹)					
biochar	Na	K	Mg	Ca	P
CE5s	*	*	*	*	*
RO5f	0.32	4.6	0.38	12	0.22
CS5f	0.47	18.4	4.7	15	2.8
CS3s	0.58	13.0	4.4	9.6	3.6
CS5s	0.82	24.9	4.9	12	4.3
CS6s	1.03	53.0	3.2	6.2	2.7
HW5s	0.90	2.0	0.60	23	0.29
MW6g	3.7	5.0	3.1	41	0.17
RSD (%)	22	4	17	17	20
biochar	S	Si	Mn	Fe	Al
	*	*	*	*	*
CE5s	0.05	0.59	0.05	0.09	*
RO5f	0.29	0.86	0.09	0.38	0.17
CS5f	0.34	1.4	0.07	0.68	0.31
CS3s	0.25	1.7	0.08	0.76	0.92
CS5s	0.11	1.8	0.10	0.00	0.18
CS6s	0.12	0.74	0.29	0.10	0.2
HW5s	0.79	5.8	0.20	0.00	0.67
RSD(%)	33	19	13	38	33

RSD = relative standard deviation

*below detection limit

Figure 1. Biochar structural (conjugate acid $5 \leq \text{pK}_a \leq 6.4$), other organic, carbonate ($\text{HCO}_3^- + \text{CO}_3^{2-}$), and other inorganic (non-carbonate) alkalinity in meq per gram of biochar. Error bars represent the standard deviation of the mean ($n = 3$).

Figure 2. Relationship between total soluble base cations (sum of meq g^{-1} for 0.05 M HCl extractable Na + K + Ca + Mg) and total alkalinity (meq g^{-1}) for all eight untreated biochars. Each data point represents the mean of three measurements. Total alkalinity was determined by titration of 0.05 M HCl extracts.*

*In the case of HW5s, total alkalinity was calculated as the sum of carbonate alkalinity, structural alkalinity, and other inorganic alkalinity because carbonate alkalinity (1.47 meq g^{-1}) exceeded the total titratable alkalinity (1.16 meq g^{-1}).

Figure1

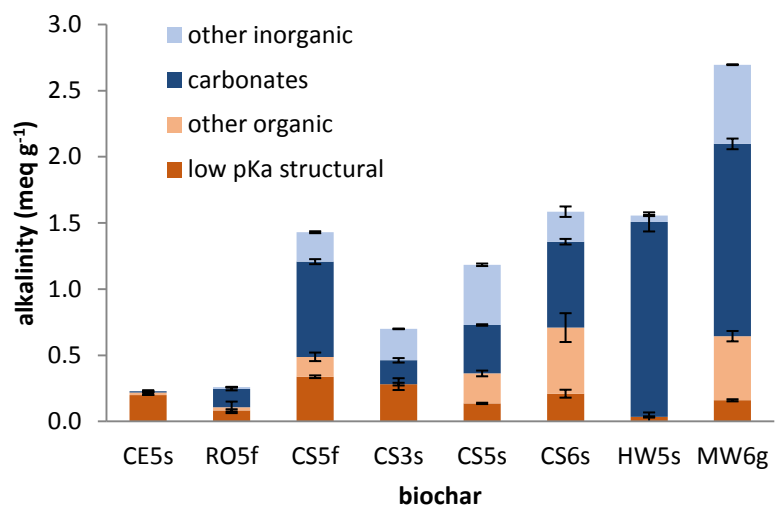


Figure2

